

NITRATE, PHOSPHATE AND FLUORIDE REMOVAL FROM WATER USING ADSORPTION PROCESS

By

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A Thesis submitted in fulfilment for the degree of

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CERTIFICATE OF AUTHORSHIP/ ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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To my father Late Md. Nurullah and mother Monju Monowara

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Nomenclature

C = the bulk phase concentration (mg/L)

$\text{Ca}(\text{OH})_2$ = Calcium hydroxide

C_e = equilibrium concentration of adsorbate (mg/L)

C_0 = initial concentration of adsorbate (mg/L)

C_o = inlet adsorbate concentration (mg/L)

C_s = the concentration on the external surface (mg/L)

C_t = concentration of adsorbate at time t (mg/L)

C_t = outlet adsorbate concentration at time t (mg /L)

Ca^{2+} = Calcium

Cl^- = chloride

CO_3^{2-} = carbonate

COD = chemical oxygen demand

CR = Chemical reduction

D_L = the axial dispersion coefficient (m^2/s)

D_m = molecular diffusion coefficient

D_s = the surface diffusion coefficient (m^2/s)

Dowex 21k XLT = strong base anion exchange resin composed of Styrene-DVB

EDR = electrodialysis reversal

ϵ_b = the bed voidage

F = Fluoride

F = linear velocity calculated by dividing the filtration velocity by the column section area (cm/min)

Fe^{3+} = iron (III)

FTIR = Fourier transform infrared spectroscopy

FeO = zero-valent iron

g/L = gram per litre

H₂PO₄⁻=dihydrogen phosphate ion

HCl = hydrochloric acid

HCO₃⁻ = bicarbonate

HFO = iron (iii) oxide

HSDM = Homogeneous surface diffusion model

H₄O₄Zr = Zirconium (IV) hydroxide

HNO₃ = Nitric acid

hr = hours

K⁺ = Potassium

k_f = the external mass transfer coefficient (m/s)

K_F = Freundlich constants (mg/g)

K_L = Langmuir constant related to the energy of adsorption (L/mg)

k_{Th} = Thomas rate constant (mL/min.mg)

k_{YN} = rate velocity constant (1/min)

k₁ = equilibrium rate constant of pseudo-first-order sorption (1/min)

k₂ = equilibrium rate constant of pseudo-second-order (1/min)

k_{AB} = kinetic constant, (L/mg.min)

KNO₃ = Potassium nitrate

KH₂PO₄ = Monopotassium phosphate

KCl = Potassium chloride

LDHs = layered double hydroxides

M = mass of dry adsorbent (g)

MBR = membrane bioreactor

mg N/L = milligram nitrogen per litre

mg NO₃⁻ / L = mg nitrate per litre

mg N/g = milligram nitrogen per gram

mg P/L = milligram phosphorus per litre

mg PO₄³⁻ / g = mg phosphate per gram

mg P/g = milligram phosphorus per gram

mg F/L = milligram fluoride per litre

mg F/g = milligram fluoride per gram

min = minutes

mL/min = millilitre per minute

m/h = meter per hour

MgCl₂.6H₂O = Magnesium Chloride Hexahydrate

Mg⁰ = zero-valent magnesium

μ = Solution viscosity

N = nitrogen

Na⁺ = sodium

NaCl = sodium chloride

NaF = sodium fluoride

NaOH = sodium hydroxide

Na₂SO₄ = sodium sulphate

Na₂CO₃ = sodium carbonate

NaHCO₃ = sodium bicarbonate

NaNO₃ = sodium nitrate

NO₃⁻ = nitrate

(NH₄)₂SO₄ = ammonium sulphate

N_o = saturation adsorbate concentration (mg/L)

n = Freundlich constant

Pe_L = Peclet number for axial dispersion

Pe_m = Peclet number for particle

ρ_p = the apparent density of the adsorbent, kg/m³

P = phosphorus

pH = measure of the acidity or basicity of an aqueous solution

Purolite A520E = macroporous strong base anion exchange resin

Purolite A500PS = macroporous strong base anion exchanger consists of styrene-divinylbenzene with a trimethylamine functional group

Purolite FerrIX A33E = hybrid strong base anion exchange resin with quaternary ammonium functional groups blended with hydrous iron oxide

PZC = point of zero charge

Q = Flow rate (cm³/s)

q = surface concentration at any radial distance (r) (mg /g)

q_e = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

q_{max} = maximum amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

q_o = equilibrium adsorbate uptake per g of adsorbent (mg/g)

R = the particle radius of adsorbent (m)

RO = reverse osmosis

rpm = Revolutions per minute

Sc = Schmidt number and

SEM = Scanning electron microscopy

SO_4^{2-} = sulphate

t = filtration time (min).

τ = the time required for 50% adsorbate breakthrough (min)

t = the time (min)

τ = the tortuosity

V = volume of the solution (L)

V = the interstitial velocity (m/s)

V_s = superficial velocity (m/s)

z = the axial coordinate (m)

XRD = X-ray diffraction

XPS = X-ray photoelectron spectroscopy

Z = bed depth of column (cm)

ZVI = Zero-valent iron

Abstract

The wastewater treatment industry has identified the discharge of inorganic anions such as nitrate, phosphate and fluoride into waterways as a risk to the natural environment and human health. Of the various methods for removing these anions, adsorption/ion exchange methods are promising because they are simple, efficient, economical and result in less sludge production and therefore experience minimal disposal problems.

Of the four ion exchange resins tested (Purolite A520E, Purolite A500PS, Purolite FerrIX A33E and Dowex 21k XLT), Purolite A520E emerged as the most efficient adsorbent, having a high adsorption capacity for the removal of nitrate from water. Purolite A520E proved to be the most efficient at removing nitrate (84%) followed by Dowex 21k (81%), and Purolite A500PS (75%) within 120 min. The lowest removal efficiency was found for Purolite FerrIX A33E (48%). The Langmuir adsorption capacity was 33 mg N/g for this resin and the highest column adsorption capacity was 21.3 mg N/g at an inlet concentration of 20 mg N/L, 12 cm bed height and 2.5 m/h filtration velocity. The kinetics of nitrate adsorption by Purolite A520E in the batch study was satisfactorily described using pseudo-first-order, pseudo-second-order and HSDM models. The experimental and Thomas models predicted breakthrough adsorption capacities (12.0-13.5 mg N/g and 8.2-9.7 mg N/g, respectively) agreed fairly well. The presence of other co-ions such as SO_4^{2-} , F^- , Cl^- and PO_4^{3-} did not compete much with nitrate at equal concentrations for adsorption on Purolite A520E; only high concentrations reduced the effectiveness of this resin's ability to adsorb nitrate. Moreover, at all nitrate to phosphate ratios in solution, the ratio of nitrate to phosphate adsorbed was higher for Purolite A520E which suggested that the nitrate selectivity for adsorption was higher than phosphate. It was found that solution pH had little effect on nitrate adsorption in the pH

range 5-8. Moreover, Purolite A520E was regenerated and used at least three times without significantly reducing the adsorption capacity.

Of the six adsorbents tested in a batch study (Purolite A520E, Purolite A500PS, Purolite FerrIX A33E, Dowex 21k XLT, HFO (iron (iii) oxide HFeO_2) and Zirconium (IV) hydroxide ($\text{H}_4\text{O}_4\text{Zr}$)), Purolite FerrIX A33E had the highest phosphate removal efficiency (98%) followed by Dowex 21k (91%), Zirconium (IV) hydroxide (89%), Purolite A500PS (75%) and Purolite A520E (69%) within 240 min. HFO was found to have the least removal efficiency (36%). The batch adsorption isotherm data for Purolite FerrIX A33E was satisfactorily explained using the Langmuir, Freundlich and Tempkin isotherm models. Meanwhile the kinetic adsorption data fitted reasonably well to the pseudo-second-order, Elovich and intraparticle diffusion models. The Langmuir maximum adsorption capacity of Purolite FerrIX A33E was 48 mg P/g which constituted one of the highest phosphorus adsorption capacities reported in the literature. Three empirical models - Bohart-Adams, Thomas and Yoon-Nelson - and a numerical model based on the advection-dispersion equation satisfactorily described phosphate adsorption behaviour in a fixed-bed column containing Purolite FerrIX A33E. The phosphate adsorption capacity of the column was estimated by: firstly, the Thomas model to be 22.7 mg P/g; and secondly, the breakthrough curve calculation to be 16.3 mg/g at the inlet concentration of 30 mg P/L, 12 cm bed height and 10 m/h filtration velocity. pH had little effect on phosphate adsorption by Purolite FerrIX in the pH range 4 – 10.

The decreasing order of the anions' competition with phosphate was as follows: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$. The Purolite FerrIX A33E resin was regenerated by leaching the adsorbed phosphate with 1 M NaOH solution and reused at least four times without significantly reducing the adsorption capacity. This phosphorus desorbed was recovered as struvite by adding magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and ammonium sulphate

(NH₄)₂SO₄ at the molar ratio of phosphate, ammonium and magnesium of 1:1:1. Calcium hydroxide (Ca (OH)₂) was added to the desorbed solution to recover phosphorus as hydroxyapatite at the molar ratio of phosphate and calcium of 1:0.5 and 1:2. The XRD and FTIR analyses confirmed the recovered compounds were struvite and hydroxyapatite. These compounds' phosphorous content was 12-14% which was similar to the phosphorus content of struvite and hydroxyapatite.

Hydrous ferric oxide (HFO) had the highest fluoride adsorption capacity of seven adsorbents tested (Purolite A520E, Purolite A500PS, Purolite FerrIX A33E, Dowex 21k, HFO (iron (iii) oxide HFeO₂), Zirconium (IV) hydroxide (H₄O₄Zr) and α -Alumina (Al₂O₃)). Among the seven adsorbents, HFO had the highest fluoride removal efficiency (56%) followed by Dowex 21k (52%), Zirconium (IV) hydroxide (38%), Purolite A502PS (35%), Purolite FerrIX A33E (29%) and Purolite A520E (25%) within 120 min. The lowest removal efficiency was found for α -Alumina (4%). The batch adsorption of fluoride on HFO was satisfactorily explained using both the Langmuir and Freundlich isotherms while the column adsorption data fitted reasonably well to the Thomas model. However, by using an artificial neural network approach the model's capability did improve. The Langmuir maximum adsorption capacity at pH 6.5 was 6.71 mg F/g and the highest column breakthrough adsorption capacity was 7.06 mg F/g at the inlet concentration of 30 mg F/L, 12 cm bed height, pH 5 and 2.5 m/h filtration velocity. The adsorption capacity predicted by the Thomas model was also highest (12.7 mg F/g) for these experimental conditions. The kinetic data concerning the fluoride adsorption on HFO was better described with the pseudo-second-order model compared to the pseudo-first-order model. The HFO was regenerated by leaching the adsorbed fluoride with 0.1 M NaOH solution and reused for at least three times. However, the fluoride adsorption capacity declined with repeated use.

